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Anaerobic digestion of C_1–C_4 light oxygenated organic compounds derived from the torrefaction of lignocellulosic materials

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ABSTRACT

This paper reports the anaerobic digestion (AD) of the aqueous phase rich in C_1–C_4 oxygenated organic compounds derived from the torrefaction of six lignocellulosic materials (corn stover, annual rye straw pellet, pea hay, sorghum biomass, arundo donax and red fir wood) in an Auger reactor. The content of some of the most important C_1–C_4 compositions found in the aqueous phase measured by GC/MS is reported. Some of the compounds identified in the torrefaction aqueous phase produced (acetic acid, acetol, hydroxyacetaldehyde and phenol 2-methoxy) were anaerobically digested. The optimal concentration at which acetol and acetic acid could be digested was 1.5 and 1 mass % respectively. Much lower optimal concentrations were obtained for hydroxyacetaldehyde (HAA) and phenol 2-methoxy (0.01 mass %) which were found to be the main inhibitors. At 200 h and at the optimal concentration obtained for acetic acid, acetol, HAA and phenol-2 methoxy the yield of biogas produced was 363, 50, 600 and 4100 ml/g respectively. The AD of the aqueous phase obtained from the torrefaction of the six biomasses studied was conducted at the same conditions used for the model compounds. The optimal concentration these aqueous phases could be digested was: 2.5, 1.5, 1.5, 1.5, 0.5 and 0.5 mass % for the pea hay, corn stover, arundo donax, annual rye, sorghum biomass and red fir wood respectively. At 500 h and the optimal concentrations the yield of bio-gas produced was 106, 85, 91, 53, 32 and 88 ml/g of aqueous phase for pea hay, corn stover, arundo donax, annual rye straw, sorghum biomass and red fir wood respectively. A linear correlation was obtained between the optimal concentration at which a torrefaction aqueous phase can be AD and the content of HAA + phenols.

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1. Introduction

The torrefaction of lignocellulosic materials is currently being studied as a pathway to reduce the grinding energy of lignocellulosic materials and in this way facilitate the grinding of these materials in ball mills available in pulverized coal power plants [1,2]. Torrefaction is an anaerobic thermal treatment in the relatively low temperature range of 225–300 °C [3–5]. The main aim of this technology is to produce a fuel with increased energy density and with brittle structure that dramatically decrease the required energy necessary for grinding [1,2]. Torrefaction induces the degradation of hemicellulose and amorphous cellulose and modifications in the structure of crystalline cellulose and lignin [1,6]. During the torrefaction/pyrolysis of lignocellulosic materials 8 to 15 wt.% of the dry feedstock is converted into light oxygenated organic compounds with between one and four carbon atoms with little economic value [3,7]. Acetic acid, propionic acid, formic acid, methanol, hydroxyacetaldehyde (HAA) and acetol are the main C_1–C_4 compounds produced during anaerobic thermal pretreatment processes [3,7,8]. In most of the existing torrefaction technologies the volatiles containing these compounds are combusted with little positive effect on the overall efficiency and economic viability of the unit.

In the 19th century, refining aqueous fractions from hardwood slow pyrolysis was the main source for methanol, acetic acid and acetone [9]. The development of cheaper catalytic routes to produce methanol, acetic acid and acetone in the first half of the 20th century [10,11] is the main reason for the current lack of interest in producing and utilizing biomass derived light oxygenated organic compounds. Furthermore, the production of these light oxygenated organic compounds from pyrolysis and torrefaction is considered an environmental problem and a major hurdle for the commercialization of pyrolysis/torrefaction technologies due to the lack of technologies allowing their disposal or valorization [9].

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Table 1
Composition of lignocellulosic materials studies (mass %).

	Corn stover	Annual rye straw pellet	Pea hay	Sorghum biomass	Arundo donax	Red fir wood chips
Glucose	28.74	43.44	33.92	20.21	18.52	56.96
Galactose	0.49	0.91	2.73	0.39	0.80	3.70
Arabinose	1.17	2.21	1.39	0.72	1.65	1.08
Mann/xylose	6.61	9.95	4.29	4.44	7.28	14.93
Acid insoluble lignin	37.24	30.97	20.07	35.82	25.22	11.07
Acid soluble lignin	2.79	2.32	6.50	2.96	7.79	1.25
Extractives	1.52	3.45	2.08	6.66	10.32	4.20
Ash	6.51	6.46	10.92	4.37	5.29	0.34

There are very few studies on the valorization of C_1–C_4 molecules derived from biomass torrefaction. Most of the studies reported in the literature deal with the separation C_1–C_4 molecules derived from the pyrolysis of lignocellulosic materials [12,13]. The separation of an aqueous phase rich in C_1–C_4 molecules from the C5+ molecules produced during pyrolysis is typically conducted in fractional condensers [13]. The heavy bio-fuel precursors are collected in the first condenser which typically operates around 80 °C where they can be further upgraded to higher value fuels [13]. Several studies have been published on the valorization of the C_1–C_4 molecules produced during biomass pyrolysis [14–20]. Some of the studies have reported a concept of hydrogen production derived from these molecules via thermochemical conversion. To the best of our knowledge, this is the first paper reporting the anaerobic digestion (biological conversion) of C_1–C_4 molecules derived from biomass torrefaction.

Many coal combustion companies are currently studying the possibility of combusting torrefied biomass in power plants. These companies are interested in understanding whether higher value products or disposal strategies for the C_1–C_4 molecules produced during the torrefaction step are possible. Thus, in this paper we study the anaerobic digestion of aqueous phases rich in C_1–C_4 molecules produced from the torrefaction of six biomasses with the objective to determine the optimal concentration (for highest biogas production). The toxic compounds controlling the maximum quantity of torrefied aqueous phase that can be anaerobically digested will be investigated.

2. Materials and methods

2.1. Feedstocks and their composition

Corn stover, annual rye straw pellet, arundo donax, pea hay, sorghum biomass and red fir wood chips were kindly provided from the Portland General Electric Company (Portland, OR). The content of extractives, ash, carbohydrate and lignin of each of the materials studied was determined following ASTM and NREL standard determination methods [21–23]. Briefly, the analyzed samples were sieved to obtain homogenous particle size distribution between 40 and 60 mesh. Samples weighted 300.0 ± 10.0 mg were added into a tared pressure tube. Then, the first hydrolysis step was carried out with 3 ml condensed sulfuric acid (72%) in 30 °C water bath for 60 ± 5 min with stirring every 5–10 min in each. After that, the condensed sulfuric acid in each tube was diluted by 84.00 ± 0.04 ml deionized water and the tube was inverted several times for homogenous 4% diluted sulfuric acid. The second hydrolysis step was carried out in the 121 °C autoclave for 1 h. Then, all the tubes were taken out and cooled down to room temperature before all the caps removed. G3 crucibles, which had obtained constant weight, were used to separate liquor and solid in the tubes with vacuum filter. The liquor of each tube was collected separately. After that, hot deionized water was utilized to transfer the entire solid in each tube to their corresponding crucible and wash the sample on each crucible until the pH of the used water getting through the crucible is about 7. All the crucibles were taken to an oven of 105 ± 3 °C for four hours. Klason lignin (insoluble) contents could be got by weighting the solid on the crucibles. Then, all the crucibles were put into muffle furnace 575 ± 25 °C for 24 ± 6 h. Ash content could be got by measuring solid content on the crucible later. For sugar analysis, the liquor collected was analyzed by Ion Chromatograph (Dionex ICS-3000, column: IonPac AS11-HC 4X250mm). Soluble lignin was detected by UV (Shimadzu UV-2550PC UV/Vis Spectrophotometer) at 205 nm wavelength. The extractives were measured by soxhlet extraction using ethanol/toluene as solvent. The ash content was obtained by burning the sample in the furnace at 575 °C overnight.

Table 2
Elemental analysis results (mass %, dry).

	Corn stover	Annual rye straw pellet	Pea hay	Sorghum biomass	Arundo donax	Red fir wood chips
C	47.53	49.46	49.11	46.43	46.07	49.77
H	6.83	7.35	7.83	7.13	7.07	7.19
N	0.59	0.69	2.03	0.62	2.24	0.04
Ash	6.51	6.46	10.92	4.37	5.29	0.34
O[a]	38.54	36.04	30.11	41.45	39.33	36.37

[a] By difference.

The elemental composition (CHN-O) of these samples was determined using a LECO® TruSpec CHN Analyzer (St. Joseph, MI). Approximately 0.06 g of oven dry material was combusted at 950 °C in the combustion chamber of the LECO equipment with pure oxygen instead of air.

The content of alkalines in the sample was quantified by ICP-MS (Agilent Technologies-7500 Series) with Autosampler (Agilent Technologies-ASX-500 Series). 15 mg of ash samples was digested by 6 ml of concentrated reagent grade nitric acid (50%) at 90–95 °C for 2 h. Then, digested samples were diluted into 100 ml volumetric flasks with addition of 100 μl of internal standard solutions (AccuStandard, Environmental Internal Standard Mix) for accuracy of further ICP analysis [24].

Table 3
Metal analysis results.

Metals	Units	Corn stover	Annual rye straw pellet	Pea hay	Sorghum biomass	Arundo donax	Red fir wood chips
Na	ppm	765	4159	739	360	467	4
Mg	ppm	468	1419	5119	909	933	80
K	ppm	13,008	8138	17,549	10,545	11,037	435
Ca	ppm	2393	2420	13,421	762	944	572
Fe	ppm	37	77	360	–	12	17
Al	ppb	156,071	255,778	404,463	69,637	90,440	14,739
Mn	ppb	19,401	209,056	42,164	8136	11,948	19,627
Cu	ppb	2081	3448	8712	1870	1071	807
Zn	ppb	13,039	20,986	71,716	10,619	27,659	4548
Ba	ppb	6472	27,930	30,613	5317	4039	16,605
Total	ppb	213,735	533,411	594,856	108,155	148,550	57,434

Table 4
Yield of torrefaction products (mass %).

	Corn stover	Annual rye straw pellet	Pea hay	Sorghum biomass	Arundo donax	Red fir wood chips
Aqueous phase	38.55	38.46	30.87	56.99	40.94	15.15
Torrefied solid	57.83	43.36	58.39	41.94	49.66	83.33
Gases[a]	3.61	18.18	10.74	1.08	9.4	1.52

[a] By difference.

2.2. Torrefaction of various feedstocks and characterization of the aqueous phase produced

Torrefaction of all the lignocellulosic materials studied was performed in an auger reactor [3]. Around 300 g of samples was torrefacted in the reactor at 310 °C with a residence time between 7.5 and 10.8 min. The yields of products were recorded and the composition of the obtained aqueous phase was analyzed by Karl Fischer titration (Schott Instruments TitroLine Karl Fischer Volumetric Titrator) and GC/MS (Agilent, Column: HP-5MS, 30 m × 250 μm × 0.25 μm, 7890A Gas Chromatograph with a 5975C Mass Selective Detector).

The content of selected volatile organic compounds heavier than water was measured with a GC/MS (Agilent 6890 N). The instrument was calibrated with solutions of standard (selected) compounds at five different concentrations. Methanol solutions containing 20 mass% of oil samples were prepared for the study. All of the solutions were filtered (0.45 μm) to remove bio-char particles from the sample. Filtered solutions (1 μl) were injected into the inlet at 200 °C working with a split ratio of 20:1. The vapors from the inlet were separated by capillary column (Agilent HP-5 MS, HP19091S-433) using helium as a carrier gas (1 mL/min). The column was held at 40 °C for 1 min, heated at 3 °C/min until 280 °C, and held for another 10 min at the final temperature. The mass spectrometer was operated with a transfer line temperature at 150 °C, an ion source temperature at 230 °C, and an electron impact ionization (EI) at 70 eV. The mass of the fragments obtained was scanned from 28 to 400 (amu). Each of the peaks obtained was identified with the NIST/EPA/NIH mass spectral library (Version 2.0d, Fair Com Corporation). The total organic carbon of the aqueous phase produced was determined using a Shimadzu TOC-5000 analyzer (Shimadzu, Kyoto, Japan). The test range of total carbon was 1 to 4000 ppm. All samples was diluted 40 times and filtered with a 0.45 μm filter, then injection with a 250 μL syringe into the analyzer. The total organic carbons of the aqueous phases obtained from torrefaction were quantified [25].

2.3. AD of model compounds and torrefaction aqueous phases rich in C_1–C_4 organic compounds

A dedicated 16-cell batch respirometer unit (Challenger Systems, AER-200 respirometer, Springdale, AR, USA) was utilized to study the yield of bio-methane. Acetic acid, acetol, hydroxyacetaldehyde and phenol, 2-methoxy- were selected as model compounds to study their inhibitory effects on the AD process. The bottles were prepared with an inoculum VS to substrate VS ratio of 1. Model compounds (substrate) and torrefaction aqueous phases with different concentration between 0.01 and 6% (100 ml) were added into bottles and mixed with 100 ml of inoculums (primarily sludge). The inoculums were obtained from

Table 5
Content of selected compounds in the aqueous phase produced from the torrefaction of several lignocellulosic materials (mass %).

	Corn stover	Annual rye straw pellet	Pea hay	Sorghum biomass	Arundo donax	Red fir wood chips
Water	72.43	64.41	72.38	66.04	65.12	60.96
Formic acid	0.20	0.80	0.55	0.59	0.24	2.09
HAA	0.58	0.97	0.22	0.88	0.70	0.74
Acetic acid	6.58	7.93	8.77	9.66	17.65	14.24
Acetol	3.39	4.21	2.94	2.98	2.90	4.38
Propionic acid	0.74	0.67	0.60	0.85	0.83	0.68
1-Hydroxy-2-butanone	2.39	2.57	2.22	2.80	3.58	1.69
Butanedial	0.12	0.17	0.10	0.14	0.08	0.49
Furfural (2-furaldehyde)	0.11	0.19	0.09	0.15	0.17	0.78
Acetol acetate	0.84	1.05	1.06	1.01	1.64	0.99
Furan, tetrahydro-2,5-dimethoxy-	0.40	0.44	0.33	0.49	0.34	0.61
2(5H)-furanone	0.01	0.01	0.01	0.01	0.02	0.03
Guaiacol (phenol, 2-methoxy-)	0.24	0.37	0.01	0.40	0.36	0.39
2-Furanethanol, β-methoxy-(S)-	0.01	0.01	0.00	0.01	0.00	0.04
2-Butanone, 1-(acetyloxy)-	0.11	0.13	0.13	0.17	0.21	0.26
Phenol	0.43	0.41	0.33	0.44	0.46	0.33
O-Cresol	0.01	0.01	0.00	0.01	0.01	0.00
1,2-Benzenediol, 3-methoxy-	0.21	0.23	0.21	0.25	0.22	0.27
Phenol, 4-ethyl-2-methoxy-	0.03	0.08	0.03	0.08	0.07	0.10
Syringol	0.13	0.17	0.08	0.28	0.21	0.11
Eugenol	0.00	0.00	0.00	0.01	0.00	0.08
Vanillin	0.06	0.06	0.05	0.06	0.07	0.19
1,2,4-Trimethoxybenzene	0.21	0.23	0.22	0.23	0.22	0.30
5-tert-Butylpyrogallol	0.01	0.05	0.03	0.06	0.04	0.01
2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	0.07	0.09	0.07	0.08	0.09	0.18
Levoglucosan	0.21	0.21	0.21	0.22	0.24	0.38
Phenol,4-(ethoxymethyl)-2-methoxy-	0.19	0.19	0.19	0.19	0.20	0.34
Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	0.19	0.19	0.19	0.20	0.19	0.20
Phenol, 2,6-dimethoxy-4-(2-propenyl)-	0.19	0.21	0.20	0.21	0.21	0.20
Acetosyringone	0.19	0.20	0.19	0.20	0.20	0.42
Desaspidinol	0.19	0.21	0.20	0.22	0.20	0.23
3,5-Dimethoxy-4-hydroxycinnamaldehyde	0.00	0.00	0.00	0.00	0.20	0.20
Total organic carbon	14.28	19.05	14.87	19.73	16.12	21.73

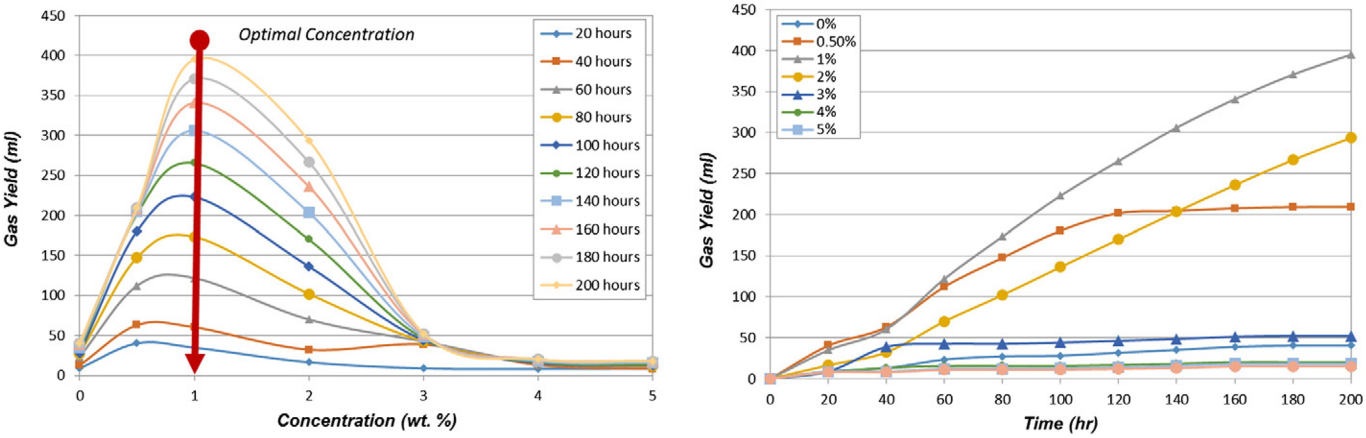

Fig. 1. AD results of selected model compound (acetic acid) at different residence times.

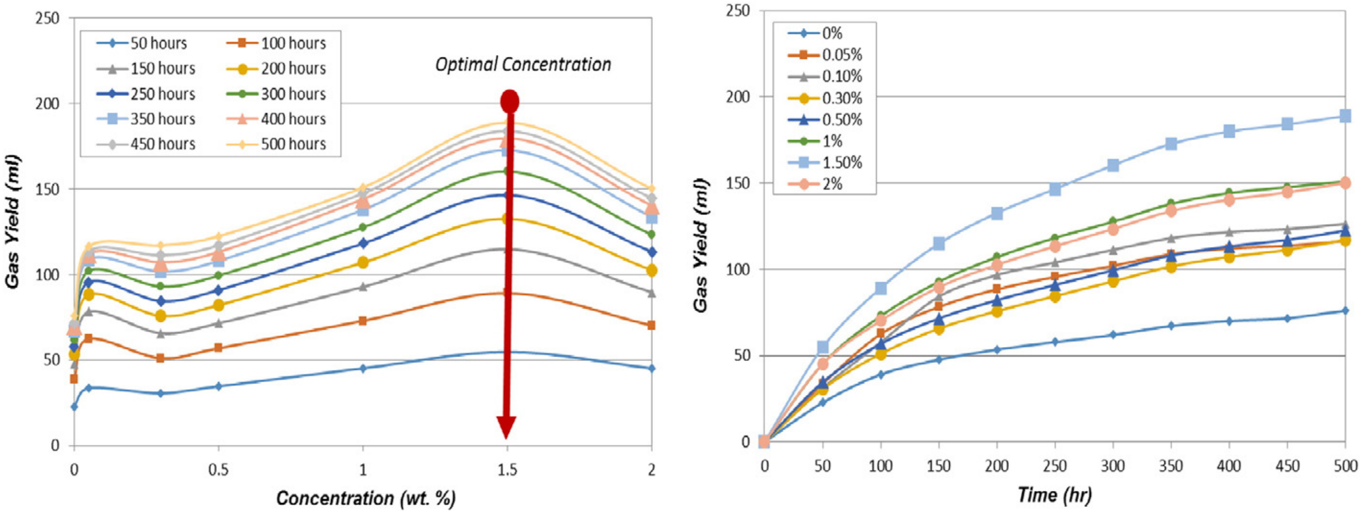

Fig. 2. AD results of selected model compound (Acetol) at different residence times.

the Pullman Wastewater Treatment Facility (Pullman, WA) in its primary anaerobic sludge digester. The studies followed classical Biochemical Methane Potential (BMP) methodology according to modified ISO protocol [26]. The BMP bottles were 250 ml in size with 50 ml of headspace and 200 ml of liquid level (digested sludge inoculum and sample). The pH value of each bottle was adjusted to 7.5–7.8 with 8% of NaOH solution before the experiment. Each bottle was magnetically stirred at a speed of 185 rpm. Sodium hydroxide was used as scrubbing media to

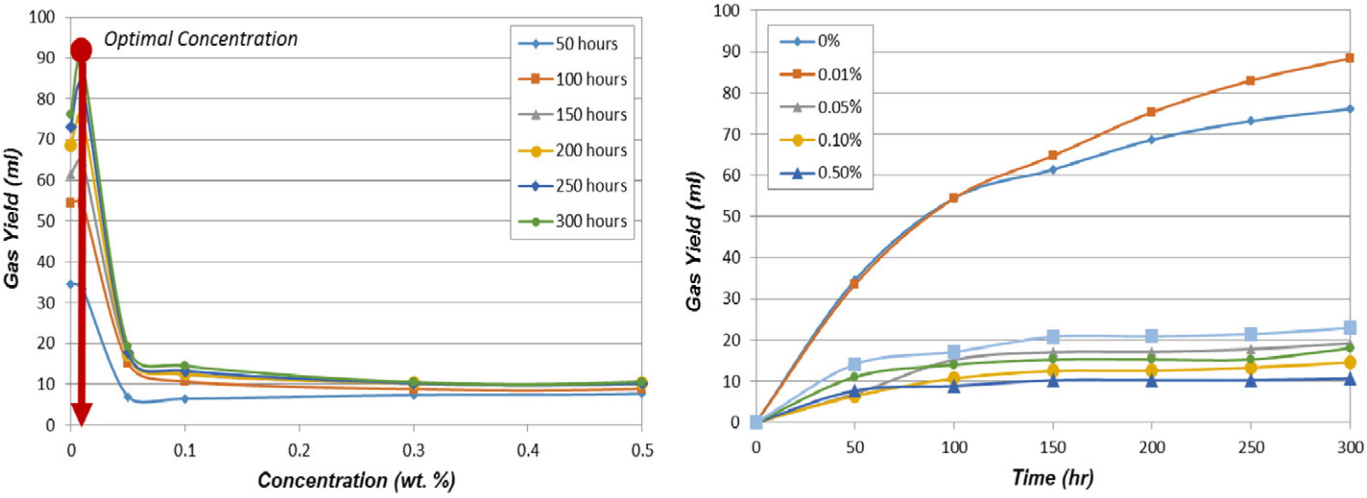

Fig. 3. AD results of selected model compound (HAA) at different residence times.

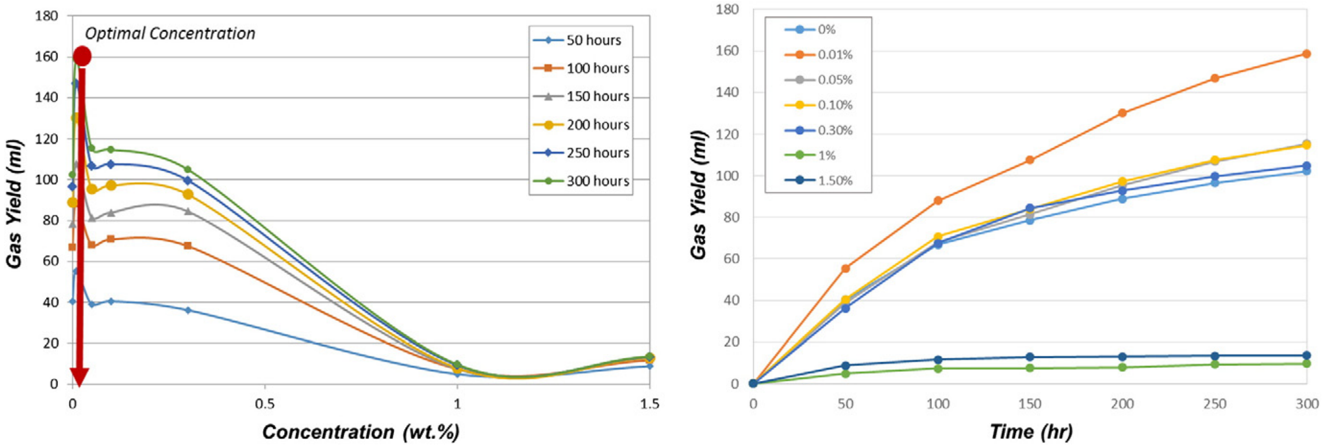

Fig. 4. AD results of selected model compound (phenol, 2-methoxy-) at different residence times.

purify CH_4 by adsorbing CO_2 and H_2S, so that only CH_4 production was recorded. The methane production was calculated by the difference between the methane produced in samples and a blank (control sludge).

3. Results and discussion

3.1. Biomass composition

The content of extractives, holocellulose (reported as glucose,arabinose, galactose and Mann/xylose), lignin and ash of all the biomass processed is shown in Table 1. Woody material (red fir wood) has much higher cellulose content than other herbaceous samples. Pea hay has the highest ash content and arundo donax has the highest extractives content.

The elemental analysis of corn stover, annual rye straw pellet, arundo donax, pea hay, sorghum biomass and red fir wood chips on dry basis are listed in Table 2. All of the samples have carbon contents between 46 and 50 mass %. The hydrogen content of all samples is around 7 mass %.

Table 3 shows the content of metals in all the materials studied. Aluminum is the most abundant metal for all the samples. Pea hay has the highest content of K, Ca, and Mg. The annual Rye straw was the material with the highest content of Na. Woody material (red fir wood) has the lowest content of almost all the earth metals due to its low ash content.

Some of these metals catalyze undesirable reactions that could lead to the formation of toxic compounds. Although the effect of these metals on the formation of toxic compounds such as the hydroxyacetaldehyde during pyrolysis is well documented [27–29], their effect during torrefaction is still unknown.

3.2. Biomass torrefaction

Table 4 shows the yield of solid residue, aqueous phase and gases produced during the torrefaction of the six materials studied at 310 °C. The yields of aqueous phases are mostly between 30 and 60 mass %. The yields of solid residue are mostly between 40 and 60 mass %. The red fir wood produces very little aqueous phase. The yield of methane that will be produced when the aqueous phase produced from this feedstock is subjected to anaerobic digested will be low.

3.3. Characterization of aqueous phase produced

Table 5 shows the composition of the liquid produced from the condensed torrefaction liquid. The total organic carbon range of aqueous phases is between 14 and 22 mass%. The chemical composition varies dramatically although all the aqueous phases studied have very high content of acetic acid (between 6.6 and 17.7 wt.%). Acetic acid is known to be an intermediate of AD processes and because of this should enhance the biogas production when digested with primarily sludge. While the potential behavior of acetic acid during AD could be predicted based on current knowledge on AD mechanisms Table 5 shows that there were some key sub-constituents (hydroxyacetaldehyde, acetol, phenols) that have possible or known AD inhibitory activities and should be further studied.

3.4. AD of model compounds (acetic acid, acetol, hydroxyacetaldehyde and phenols)

Although, it was not possible to find a study on the inhibitory effect of torrefaction products during anaerobic digestion, there are some literatures on the inhibitory effect of these compounds during lipid production and bioethanol fermentation with yeast [30,31]. These studies concluded that hydroxyacetaldehyde and phenols are the main inhibitors for yeast. So in this paper we decided to study the behavior of these compounds in anaerobic digestion. Figs. 1 and 2 show the optimal concentration of acetic acid and acetol for anaerobic digestion. These results suggest that while the optimal concentrations of acetic acid and acetol were around 1–1.5 mass %. (Fig. 3), the optimal concentration of hydroxyacetaldehyde (HAA) and phenol, 2-methoxy-(Guaiacol) (Fig. 4) compounds were close to 0.01 mass %. The high yield of methane per unit of mass obtained with hydroxyacetaldehyde and 2-methoxy phenol for very low concentration suggests that at under these conditions these compounds may have a very beneficial impact in the anaerobic digestion process of the sludge. These very high levels of methane production per unit of mass added cannot be explained by their digestion. As the concentration of these compounds increased the production of methane decreases very fast due to their inhibitory effect at high concentration. The content of these compounds in the torrefaction derived aqueous phase should be reduced as much as possible before AD. The result obtained with acetol confirm that anaerobic microbes can tolerate mild concentrations of this intermediate. The low concentration at which these model compounds can be digested (less than 1.5 wt.%) suggests that a strict control on the supply of torrefaction aqueous phases has to be established to ensure a stable digestion with sludge. Higher concentration might harm the microbial population responsible for the AD process.

Table 6
The optimal concentration of model compounds and methane production (200 h).

	Acetic acid	Acetol	HAA	Phenol, 2-methoxy
Optimal concentration (wt.%)	1	1.5	0.01	0.01
Gas production (ml/g)	363	50	600	4100

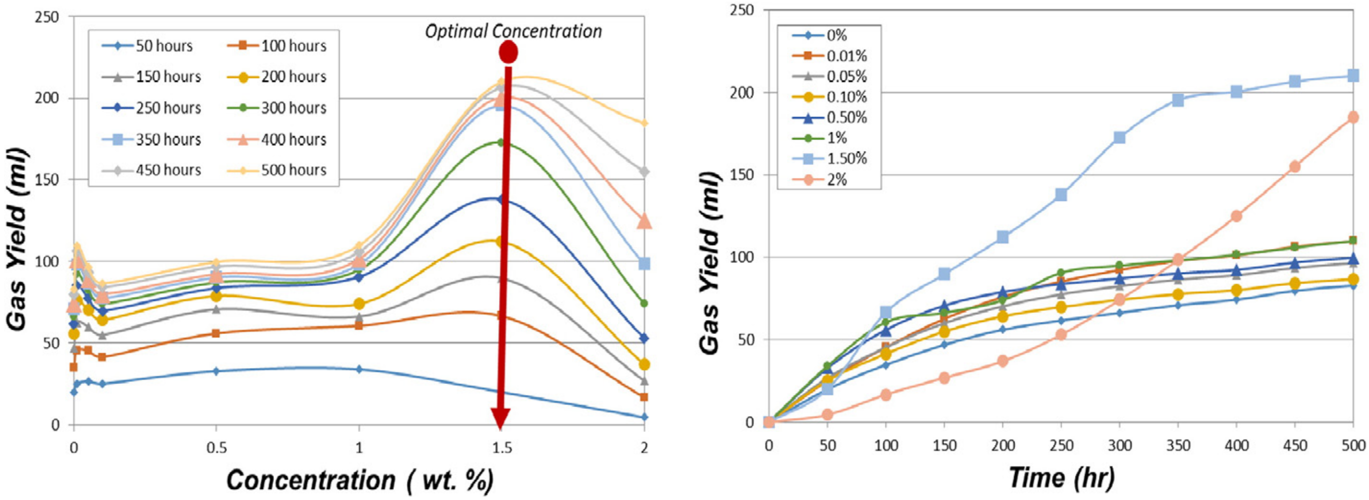

Fig. 5. AD results of torrefaction aqueous phase derived from Corn stover.

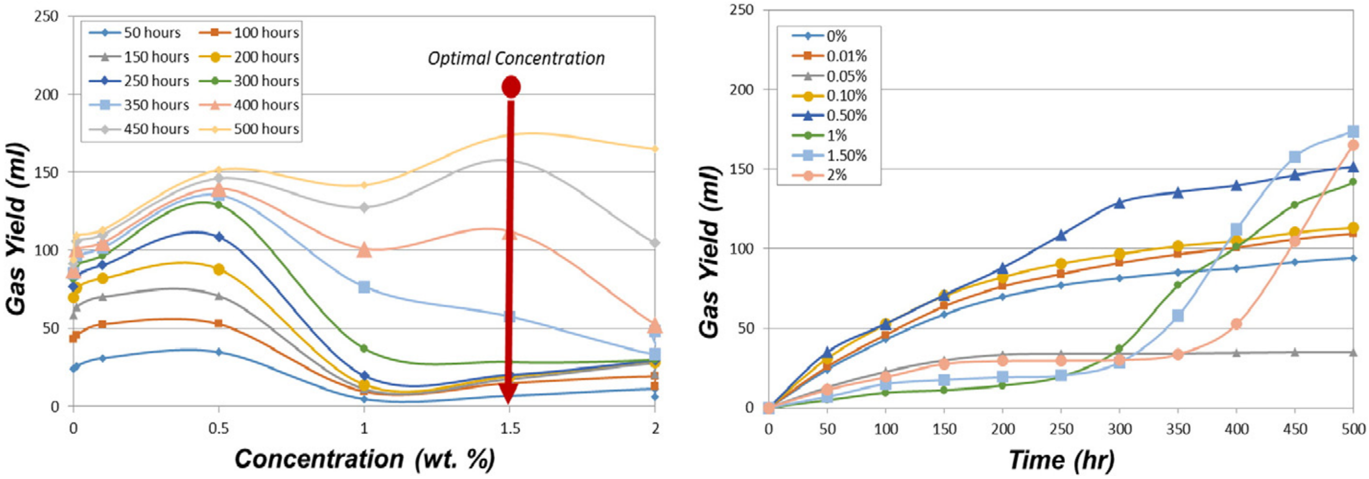

Fig. 6. AD results of torrefaction aqueous phase derived from Annual Rye straw.

Table 6 shows the optimal concentration of all model compounds with their methane production via anaerobic digestion. The highest gas production occurred when acetic acid was used as an additive to anaerobic digestion, resulting in around 363 ml of gas being produced after over 200 h of digestion (Conversion rate: 363 ml/g of acetic acid added). The yield of methane produced from HAA (6 ml) and phenol, 2-methoxy-(41 ml) were extremely low. This result suggests that HAA and phenol, 2-methoxy- are indeed toxic compounds for anaerobic

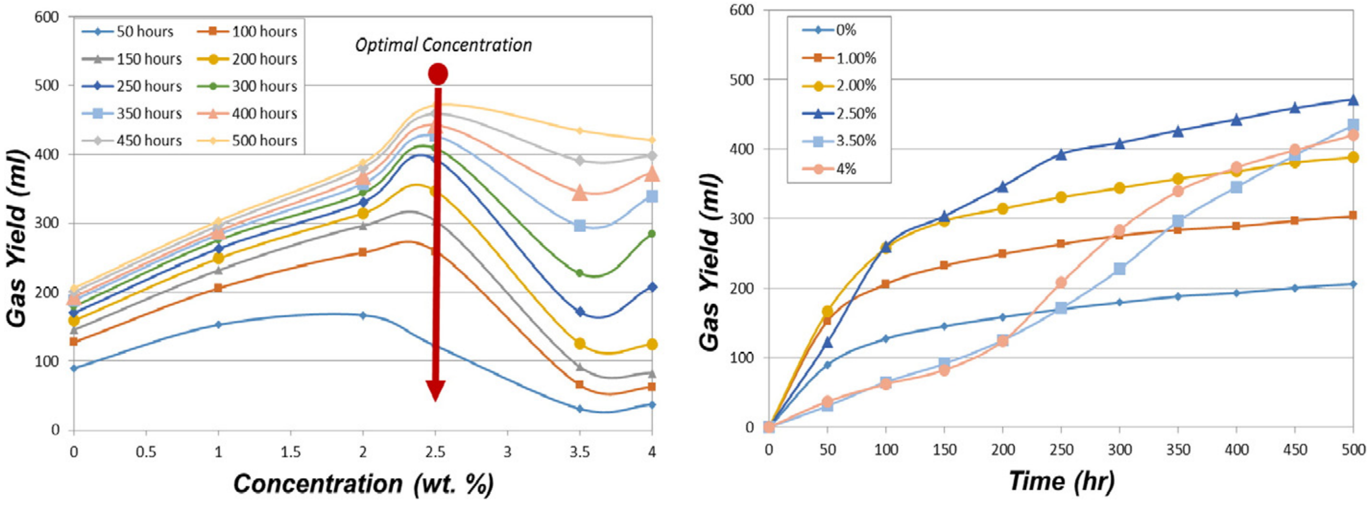

Fig. 7. AD results of torrefaction aqueous phase derived from pea hay.

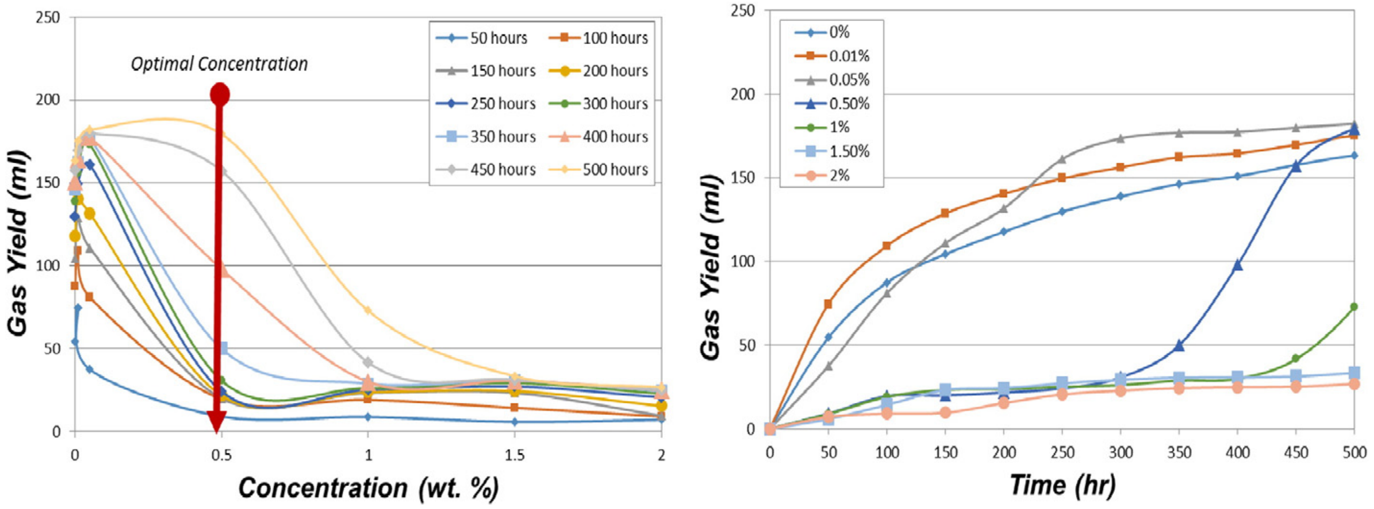

Fig. 8. AD results of torrefaction aqueous phase derived from Sorghum.

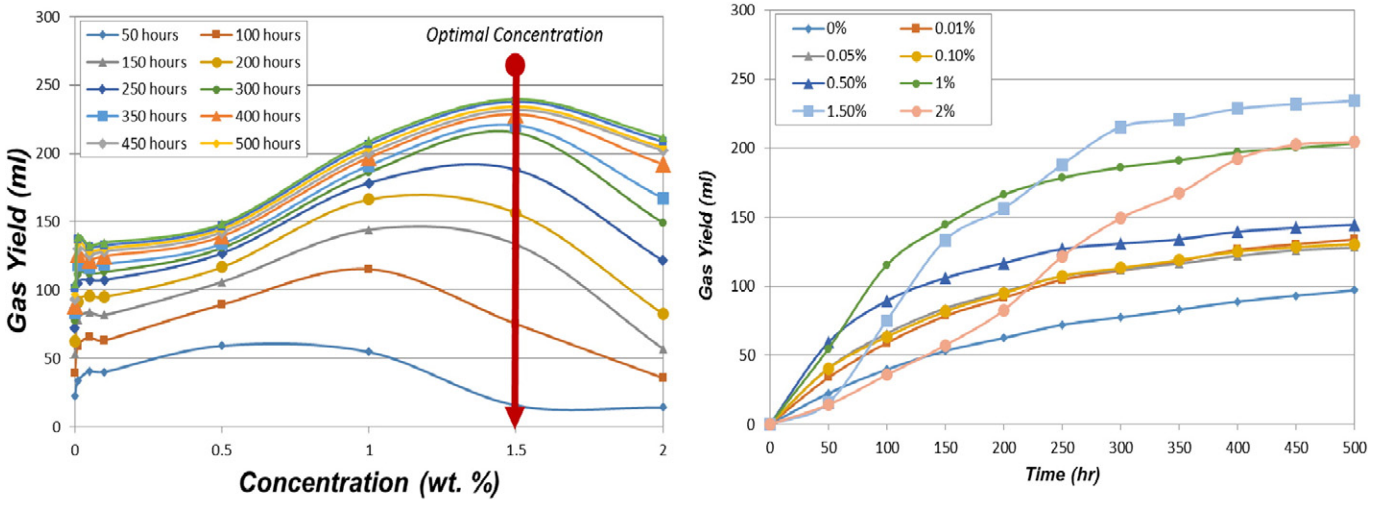

Fig. 9. AD results of torrefaction aqueous phase derived from arundo donax.

digestion. Similar results were reported for the lipid production and bioethanol fermentation by yeast [30–32]. The result also is in a good agreement with phenols being highly toxic for anaerobic digestion [33]. The complex chemical composition of the aqueous phase makes it very difficult to use the anaerobic digestion results obtained with the pure compounds to predict the AD behavior of this complex system.

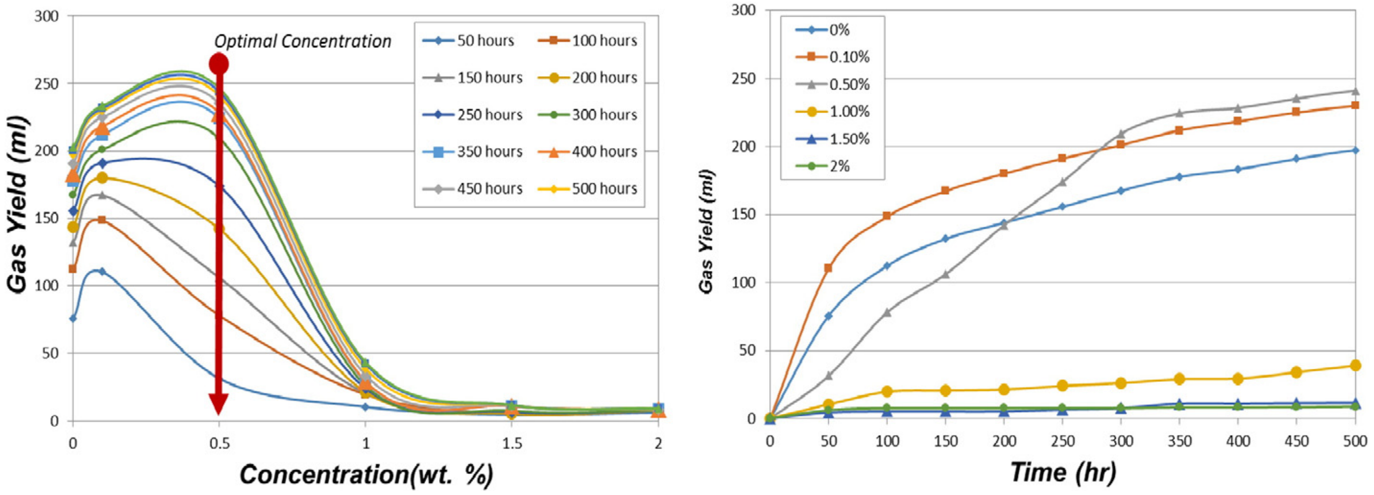

Fig. 10. AD results of torrefaction aqueous phase derived from red fir wood.

Table 7
The optimal concentration of aqueous phases and methane production (500 h).

	Corn stover	Annual rye straw pellet	Pea hay	Sorghum biomass	Arundo donax	Red fir wood chips
Optimal concentration (wt.%)	1.5	1.5	2.5	0.5	1.5	0.5
Gas production[a] (ml/g)	85	53	106	32	91	88

[a] Calculated as the difference between the methane produced in the presence of torrefaction derived aqueous phase and the methane produced by the blank (when only sludge was digested) divided by the mass of torrefied aqueous phase digested.

3.5. AD of condensed torrefaction liquids

The results of the anaerobic digestion of the aqueous phase samples studied are shown in Figs. 5–10.

Different optimal concentrations for each feedstock were observed. Of the results, the highest biogas production and highest concentration was achieved when pea hay was digested with primarily sludge. The optimal concentration increased up to 2.5% mass pea hay and the gas production achieved almost 500 ml of gas after 500 h of digestion. For the samples taken, the best substrate for AD is the aqueous phase resulted from torrefaction of pea hay. However, the optimal concentration and gas production are still lower than expected from the model compounds. The reasoning for the result may be related to the complex mechanism. There are more than ten different types of phenol compounds as known inhibitors for AD, which are found in the aqueous phase obtained from torrefaction of pea hay. Sorghum and red fir wood chips have a much lower optimal concentration than the others, but the gas yield is similar to all the other materials except pea hay. These aqueous phases contributed to the production of 200 ml of gas after 500 h.

Table 7 shows the optimal concentrations of aqueous phases obtained from various feedstocks with their methane production via anaerobic digestion. The aqueous phase obtained from torrefaction of pea hay seems to be the best additive to produce 265 ml of methane after over 500 h of digestion (Conversion rate: 106 ml/g of aqueous phase digested). The gas production in ml/g was calculated as the difference between the methane produced in the presence of torrefaction derived aqueous phase and the methane produced in the blank experiment (when anaerobically digesting the reference sludge) divided by the mass of aqueous phase digested. It is important to note that due to limitations with the number of bottles available to conduct the AD experiments, not all the tests were carried out at the same time. Several fresh blank sludges were prepared. The differences in the blank curve observed are due to the variability of the sludges collected.

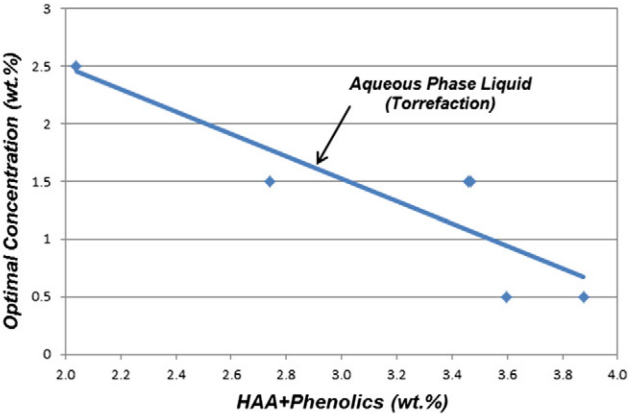

Fig. 11. Correlation between the concentration of hydroaxyacetaldehyde and phenolics in the torrefaction liquid and the optimal concentration of torrefaction aqueous phase that can be digested.

3.6. Linear correlation between toxic compounds and AD of aqueous phases

The concentration of aqueous phase liquids at which a maximum biogas production was obtained, was correlated with the content of toxic compounds (hydroxyacetaldehyde and phenolics) in the aqueous phase AD samples (see Fig. 11). A linear correlation was determined between the content of hydroxyacetaldehyde and phenols and the optimal concentration when digested with primarily sludge. This result is very important because it suggests that in order to produce an aqueous phase with a high potential for AD, it is necessary to control cellulose fragmentation reactions. These fragmentation reactions are responsible for the formation of hydroxyacetaldehyde which inhibits the AD process. Furthermore, it is important to control lignin reactions and condensation conditions to reduce the content of mono-phenols in the aqueous phase. The yield of these compounds resulted from cellulose and lignin fragmentation reactions could be controlled by the operating temperature [7]. The condensation system can also be designed to separate mono-phenols from the aqueous phase [13].

A linear correlation was also obtained between the optimal concentration of the aqueous phase digested and the maximum biogas production. Fig. 12 illustrates this relationship. This linear correlation is important because it indicates that as the content of aqueous phase (produced during torrefaction), is increased during digestion, the biogas production will also increase. Therefore, this result confirms that under the optimal digestion conditions the C_1–C_4 molecules are contributing to the formation of biogas.

4. Conclusions

This paper contributes to understand how to conduct the anaerobic digest of the aqueous phase rich in light oxygenated molecules produced during the torrefaction of lignocellulosic materials. It confirms that torrefaction aqueous phases rich in C_1–C_4 molecules can be a source for CH_4 production via anaerobic digestion with primarily sludge. Our studies prove that the concentration at which the maximum yield of biogas is produced depends on the content of hydroxyl-acetaldehyde

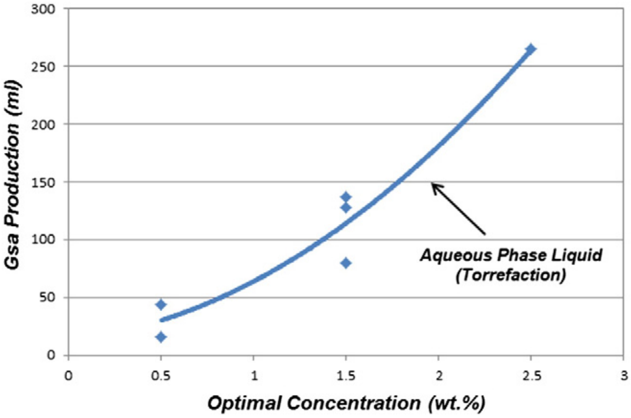

Fig. 12. Correlation between the optimal concentration of torrefaction aqueous phase processed and the maximum biogas production.

and phenols in the aqueous phase digested. A linear correlation was obtained which correlated the content of hydroxyacetaldehyde and phenols and the optimal concentration of aqueous phase that can be digested.

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